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(54) Suds suppressor compositions and their use in detergent compositions.

(57) A suds compressor composition comprising, as suds-suppressor, a blend of:

- (i) a high shear mix of polydimethylsiloxane (PDMS) and hydrophobic silica, the PDMS having a viscosity of from 20 to 12,500 cs, and
  - (ii) PDMS having a viscosity of at least 25,000 cs wherein the blend has a viscosity of at least 18,000 cs,
- the suds suppressor being dispersed in a water-soluble or water-dispersible organic carrier comprising:
- (i) from 1% to 100% of a first carrier component melting in the range from 38°C to 90°C and
  - (ii) from 0% to 99% of a second carrier component which is an ethoxylated nonionic surfactant melting in the range from 5°C to 36°C.

The compositions are particularly suitable in high-active containing heavy duty detergent compositions and provide improved foam regulation across the range of wash temperature, product usage, soil, load and rinsing conditions.

EP 0 142 910 A1

SUDS SUPPRESSOR COMPOSITIONS AND THEIR  
USE IN DETERGENT COMPOSITIONS

This invention relates to suds-suppressor compositions and to use thereof in detergent compositions. In particular, it relates to heavy duty detergent compositions having controlled sudsing characteristics especially when used in automatic washing machines for washing clothes and the like.

Detergent compositions normally contain surfactants which tend to produce foam when agitated in aqueous solution. For many applications, especially in automatic washing and dishwashing machines, excess foam production is a serious problem and with many effective surfactants, it is necessary to add foam suppressing or controlling agents in order to prevent suds-overflow from the machine or under-usage of product by the user. On the other hand, consumers normally expect and prefer a certain amount of foam to be present and, indeed, research has shown that consumers are highly sensitive to a reduction in the foam level pattern. In any particular application, therefore, the optimum degree of foaming will be sufficiently low to avoid oversudsing under all conceivable washing machine temperatures, load and soil conditions, but sufficiently high to meet the consumers preference for a moderate to generous level of foam.

Detergent compositions currently sold for the European domestic automatic washing machine market generally contain up to about 12% of organic surfactant and for such compositions, suds-suppressors satisfying the above constraints are now well established. For example, in EP-A-46342, it is taught to use a polydimethylsiloxane/hydrophobic silica suds-suppressor in the form of a dispersion in an ethoxylated nonionic surfactant using certain siloxane-oxyalkylene copolymers as dispersing agent. In EP-A- 8829, a suds-suppressor is disclosed consisting of a major portion of wax together with a nonionic dispersing agent and hydrophobic silica. GB-A- 1,407,977 discloses protection of a polydimethylsiloxane/silica suds-suppressor in a water-soluble dispersible carrier.

In detergent compositions containing a high level of surfactant, however, (in excess of about 12%) problems of foam control in front-loading automatic washing machines become increasingly intractable. Thus, the technique of dispersing

5 polydimethylsiloxane/silica in nonionic surfactant is found to become impractical at high levels of suds-suppressor because of diminishing dispersion stability. The wax/silica/dispersant systems are also found to be deficient because of their inherently slow kinetics; in other words, the rate of release of wax/silica fails to match the rate of  
10 transport of surfactant to the air/water interface. Conventional polydimethylsiloxane/silica suds-suppressors are also deficient for foam control in high active detergent compositions, presumably because the polydimethylsiloxane is rapidly dispersed or solubilized by the higher surfactant levels. Furthermore, these problems of foam control are found  
15 to be greatly exacerbated in concentrated surfactant systems containing C<sub>10-16</sub> anionic or cationic surfactants which are known to have strong foam-generating characteristics.

The present invention thus provides a suds-suppressor composition suitable for addition to a high active heavy duty detergent composition  
20 to provide improved foam control characteristics. It further provides a detergent composition containing a high level of organic surfactant and having improved foaming characteristics across the range of wash temperature conditions. It also provides a high active detergent composition containing C<sub>10-16</sub> anionic and/or cationic surfactants and  
25 having improved foaming characteristics under varying wash temperature, product usage, soil, load and rinsing conditions.

According to the present invention, there is provided a suds-suppressor composition comprising:

(a) a suds suppressor system comprising a blend of

30 (i) a high shear mix of polydimethylsiloxane and hydrophobic silica suds suppressing agents in a weight ratio of polydimethylsiloxane:hydrophobic silica in the range from about 75:25 to about 99:1, the polydimethylsiloxane having a viscosity at 25°C in the range from about 20 to about 12,500 cs, and  
35

(ii) polydimethylsiloxane suds suppressing agent having a viscosity at 25°C of at least about 25,000 cs wherein the blend of high shear mix and high viscosity polydimethylsiloxane has a viscosity at 25°C of at least about 18,000 cs, the suds suppressor system being dispersed in:

- (b) a water-soluble or water-dispersible organic carrier comprising:
  - (i) from about 1% to 100% by weight thereof of a first organic carrier component having a melting point in the range from about 38°C to about 90°C, and
  - (ii) from 0% to about 99% by weight thereof of a second organic carrier component selected from ethoxylated nonionic surfactants having a hydrophilic-lipophilic balance (HLB) in the range from about 9.5 to about 13.5 and a melting point in the range from about 5°C to about 36°C.

The suds suppressor composition thus comprises a blend of two polydimethylsiloxane components, the first component being a high shear mix of polydimethylsiloxane and hydrophobic silica wherein the polydimethylsiloxane has a viscosity of from about 20 to about 12,500 cs, and the second component being polydimethylsiloxane having a viscosity of at least 25,000 cs. The high shear mix is preferably a mixture of polydimethylsiloxane having a viscosity in the range from about 100 to about 4,000 cs, preferably from about 500 to about 2000 cs, with hydrophobic silica in a weight ratio of from about 80:20 to about 95:5. The high viscosity polydimethylsiloxane preferably has a viscosity of at least about 30,000 cs, more preferably from about 50,000 to about 100,000 cs. The blend of high shear mix and high viscosity polydimethylsiloxane, on the other hand, has a viscosity of at least about 18,000 cs, preferably at least about 20,000 cs, more preferably from about 25,000 to about 60,000 cs. The high shear mix and high viscosity silicone are generally blended in a weight ratio of from about 4:1 to about 1:4, more preferably from about 2:1 to about 1:2.

The hydrophobic silica component of the high shear mix preferably has a particle size of not more than about 100 millimicrons, more preferably from about 10 to 20 millimicrons and a specific surface area above about  $50 \text{ m}^2/\text{g}$ . The hydrophobic silica can be made, for example, by reacting fumed silica with a trialkyl chlorosilane (i.e. "silanated") to affix hydrophobic trialkylsilane groups on the surface of the silica. The hydrophobic silica is then high shear mixed with polydimethylsiloxane, the latter being end-blocked generally with trimethylsilyl or hydroxyl groups. The polydimethylsiloxane can be prepared by various techniques such as the hydrolysis and subsequent condensation of dimethyldihalosilanes, or by the cracking and subsequent condensation of dimethylcyclosiloxanes.

The high shear mix can be prepared using any conventional high shear mixing equipment. Preferably, however, mixing is performed using an in-line high shear recirculation pump such as a Janke and Kunkel. In practice, the hydrophobic silica is initially dispersed in the polydimethylsiloxane in a reservoir under low shear conditions using, for example a paddle mixer, and the dispersion is then continuously drawn-off and circulated via the high shear pump back into the reservoir until bulk homogeneity is achieved. Shear conditions in the pump are generally such that in a single pass, the temperature of the dispersion leaving the pump is raised from ambient to a temperature in excess of about  $95^\circ\text{C}$ , preferably in excess of about  $110^\circ\text{C}$ . Although a single pass under high shear turbulent flow conditions is normally adequate, nevertheless, to achieve bulk homogeneity mixing is generally continued until the temperature of the dispersion in the reservoir itself exceeds about  $95^\circ\text{C}$ . The viscosity of the dispersion also rises to some extent during the high shear mixing step. Thus in preferred embodiments employing polydimethylsiloxane of viscosity from about 500cs to about 2000cs, high shear mixing raises the viscosity into the range from about 6000 to about 10,000 cs.

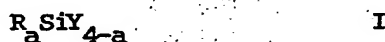
The suds-suppressor compositions of the invention comprise the suds-suppressor system in the form of a dispersion in a water-soluble or water-dispersible organic carrier. The carrier comprises from about 1% to about 100% of a first carrier component having a melting point in the range from about  $38^\circ\text{C}$  to about  $90^\circ\text{C}$ , preferably from about  $38^\circ\text{C}$  to

about 60°C, more preferably from about 40°C to about 55°C, and from 0% to about 99% of a second carrier component selected from ethoxylated nonionic surfactants having a hydrophilic-lipophilic balance (HLB) in the range from about 9.5 to about 13.5 and a melting point in the range from about 5°C to about 36°C. The weight ratio of the first organic carrier component to suds-suppressor system is from about 10:1 to 1:5, preferably from about 4:1 to 1:2, more preferably from about 2:1 to 1:1. A preferred first organic carrier component comprises ethoxylated nonionic surfactant having an HLB in the range from about 15 to about 19, preferably from about 17 to about 19. Suitable nonionic surfactants are the condensation products of the primary or secondary alcohols having from about 15 to about 24 carbon atoms, in either straight or branched chain configuration, with from about 14 to about 150, preferably from about 20 to about 100, more preferably from about 35 to about 100 moles of ethylene oxide per mole of aliphatic alcohol. Examples of surfactants of this type are the condensation products of hardened tallow alcohol with an average of between about 20 and about 100 moles, preferably about 80 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms. Other suitable organic carriers include polyethyleneglycols having a molecular weight of from about 400 to about 40,000, preferably from about 1500 to about 10,000, C<sub>12-24</sub> fatty acids and esters and amides thereof, polyvinylpyrrolidone of molecular weight in the range from about 40,000 to about 700,000 and mixtures thereof. In the case of mixtures, however, the first organic carrier component preferably comprises at least about 35%, more preferably at least about 45% of ethoxylated nonionic surfactant in order to promote transport of suds suppressor to the air/water interface.

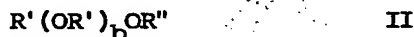
The melting point of the organic carrier components is taken herein to refer to the temperature at which melting is completed. Conveniently this temperature can be determined by thermal analysis using a Dupont 910 Differential Scanning Calorimeter with Mechanical Cooling Accessory and R90 Thermal Analyser as follows. A 5-10 mg sample of the material containing no free water or solvent, is encapsulated in a hermetically sealed pan with an empty pan as reference. The sample is initially

heated until molten and then rapidly cooled (at about 20-30°C/min) to -70°C. Thermal analysis is then carried out at a heating rate of 10 C/min using sufficient amplification of  $\Delta T$  signal (i.e. temperature difference between sample and reference - vertical axis) to obtain an endotherm-peak signal:baseline noise ratio of better than 10:1. The melting completion temperature is then the temperature corresponding to the intersection of the tangential line at the steepest part of the endotherm curve at the high temperature end of the endotherm, with the horizontal line, parallel to the sample temperature axis, through the highest temperature endotherm peak.

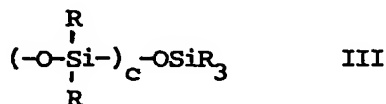
In preferred embodiments, the suds-suppressor compositions of the invention also comprise a siloxane-oxyalkylene copolymer dispersing agent which provides improved homogeneity of the polydimethylsiloxane and silica components within the organic carrier. The dispersing agent is generally added at a weight ratio with respect to polydimethylsiloxane of from about 1:4 to about 1:40, preferably from about 1:6 to about 1:20. The siloxane-oxyalkylene copolymer dispersing agent suitable for use herein has the general formula I:



wherein a is 0 or an integer from 1 to about 3, R is an alkyl group containing from 1 to about 30 carbon atoms, or a group of formula II:

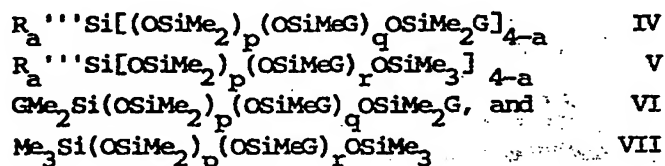


wherein R' is an alkylene group containing from 1 to about 6 carbon atoms, b has a value of from 1 to about 100, preferably from 10 to 30; and r'' is a capping group which can be selected from hydrogen, alkyl, acyl, aryl, alkaryl, aralkyl or alkenyl groups containing up to about 20 carbon atoms, sulfate, sulfonate, phosphate, carboxylate, phosphonate, borate or isocyanate groups, or mixtures thereof; Y is a group having the formula III:-



wherein R is as defined above and c has a value from 1 to about 200; and wherein at least one R group in the compound has the formula II.

Preferred dispersing agents of the above type are selected from copolymers having the general formulae IV to VII:



wherein R''' is a C<sub>1-10</sub> alkyl group, Me is methyl, G is the group of formula II, a has a value of 0 or 1, p has a value of at least 1, q has a value of 0 to about 50 and r has a value of 1 to about 50. Preferred dispersants contain G groups in non-terminal positions and contain a mixture of oxyethylene and oxypropylene groups, particularly in about a 1:1 ratio. Highly preferred are dispersants of formula VII having p+r from about 30 to about 120 with the ratio p:r from about 2:1 to about 8:1.

The suds suppressor compositions of the invention are of two main types - a granular composition wherein the organic carrier consists essentially completely of the first carrier component; and a liquid or liquifiable composition wherein the organic carrier comprises from about 1% to about 50%, preferably from about 2% to about 25% of the first carrier component and from about 50% to about 99% preferably from about 75% to about 98% of the second carrier component. In the latter instance the first carrier component is critical for storage stability of the suds-suppressor composition.

The granular suds-suppressor composition herein preferably also comprises from about 25% to about 95% thereof, more preferably from about 50% to about 85% thereof of a solid water-soluble or dispersible inorganic diluent. Suitable inorganic diluents include alkali metal, alkaline earth metal and ammonium sulphates and chlorides, neutral and acid alkali metal carbonates, orthophosphates and pyrophosphates, and alkali metal crystalline and glassy polyphosphates. A preferred inorganic diluent is sodium tripolyphosphate. Suitable water-insoluble



but dispersible diluents include the finely-divided natural and synthetic silicas and silicates, especially smectite-type and kaolinite-type clays such as sodium and calcium montmorillonite, kaolinite itself, aluminosilicates, and magnesium silicates and fibrous and microcrystalline celluloses.

In terms of processing, the granular suds-suppressor compositions are preferably made by forming a melt of the first organic carrier component, adding the high shear mix and the high viscosity silicone, preferably as a premix, to the melt, subjecting the melt to high shear mixing, adding the silicone-oxyalkylene copolymer dispersing agent, and agglomerating the melt with the inorganic diluent in, for example, a pan agglomerator, fluidized bed, Schugi mixer or the like. A preferred inorganic diluent is sodium tripolyphosphate. The particle size of the resulting agglomerate is preferably from about 0.5mm to about 2mm, especially from about 0.84 to about 1.4mm. Critically, the high shear mix of polydimethylsiloxane and hydrophobic silica having a viscosity of from about 20 to about 12,500 cs must be preformed prior to admixture with high viscosity silicone.

The liquid or liquifiable suds suppressor compositions on the other hand, are preferably made by mixing the first and second organic carrier components and, if present, the siloxane-oxyalkylene copolymer dispersing agent, premixing the high shear mix and high viscosity silicone, and high shear mixing the premix with the organic carrier.

The granular suds-suppressor compositions of the invention are normally incorporated in a granular detergent composition at a level of from about 0.1% to about 10%, preferably from about 0.5% to about 5% thereof. The liquid or liquifiable suds-suppressor compositions, on the other hand, are normally incorporated at a level in the range from about 0.5% to about 30%, preferably from about 3% to about 20% by weight of composition. The detergent compositions herein generally contain in total from about 3% to about 60% preferably from about 12% to about 50%, more preferably from about 14% to about 30% of non-soap detergent, organic surfactant selected from anionic, nonionic, ampholytic, zwitterionic and cationic surfactants and mixtures thereof. Surfactants useful herein are listed in US-A- 4,222,905 and US-A-

4,239,659. Preferred detergent compositions comprise base granules constituting from about 30% to about 99.5% by weight of composition which in turn comprise from about 3% to about 30%, preferably from about 5% to about 20% by weight of composition of non-soap organic surfactant selected from anionic surfactants, cationic surfactants and mixtures thereof. The base granules will generally also contain a detergency builder as discussed below.

The anionic surfactant can be any one or more of the materials used conventionally in laundry detergents. Suitable synthetic anionic surfactants are water-soluble salts of alkyl benzene sulphonates, alkyl sulphates, alkyl polyethoxy ether sulphates, paraffin sulphonates, alpha-olefin sulphonates, alpha-sulpho-carboxylates and their esters, alkyl glyceryl ether sulphonates, fatty acid monoglyceride sulphates and sulphonates, alkyl phenol polyethoxy ether sulphates, 2-acyloxy alkane-1-sulphonate, and beta-alkyloxy alkane sulphonate.

A particularly suitable class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts or organic sulphuric reaction products having in their molecular structure an alkyl or alkaryl group containing from about 8 to about 22, especially from about 10 to about 20 carbon atoms and a sulphonic acid or sulphuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic detergents are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the  $C_{8-18}$ , preferably the  $C_{10}-C_{16}$  fatty alcohols and sodium and potassium alkyl benzene sulphonates, in which the alkyl group contains from about 9 to about 15, especially about 11 to about 13, carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in US-A-2,220,099 and US-A-2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulphonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as  $C_{11.8}$  LAS, and  $C_{12}-C_{15}$  methyl branched alkyl sulphates.

Other anionic detergent compounds herein include the sodium C<sub>10-18</sub> alkyl glyceryl ether sulphonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride

5 sulphonates and sulphates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulphate containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

10 Other useful anionic detergent compounds herein include the water-soluble salts or esters of alpha-sulphonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulphonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the  
15 alkane moiety; alkyl ether sulphates containing from about 10 to 18, especially about 10 to 16 carbon atoms in the alkyl group and from about 1 to 12, especially 1 to 6, more especially 1 to 4 moles of ethylene oxide; water-soluble salts of olefin sulphonates containing from about 12 to 24, preferably from about 14 to 16 carbon atoms, especially those made  
20 by reaction with sulphur trioxide followed by neutralization under conditions such that any sultones present are hydrolysed to the corresponding hydroxy alkane sulphonates; water-soluble salts of paraffin sulphonates containing from about 8 to 24, especially 14 to 16 carbon atoms, and beta-alkyloxy alkane sulphonates containing from about 1 to 3  
25 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes.  
30 Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulfonate and sulfate surfactants in a weight ratio of from about 5:1 to about 1:5, preferably from about 5:1 to about 1:1, more preferably from about 5:1 to about 1.5:1. Especially preferred is a mixture of an alkyl benzene sulfonate having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, the cation being an alkali metal, preferably sodium; and either an alkyl sulfate having from 10 to 16 carbon atoms in the alkyl radical or an ethoxy sulfate having from 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6, the cation being an alkali metal, preferably sodium.

The nonionic surfactants useful in the present invention both as detergent and as the second organic carrier component are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from about 9.5 to 13.5, preferably from about 10 to about 12.5. The hydrophobic moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 14 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 9 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 11 moles of ethylene oxide per mole of phenol; nonylphenol and di-isooctylphenol condensed with 13 moles of ethylene oxide.
2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched

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5 chain configuration, with from 2 to about 12 moles, preferably 2 to about  
9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic  
alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with  
between 2 and 9, desirably between 3 and 8 moles of ethylene oxide per  
10 mole of aliphatic alcohol. The preferred surfactants are prepared from  
primary alcohols which are either linear (such as those derived from  
natural fats or, prepared by the Ziegler process from ethylene, e.g.  
myristyl, cetyl, stearyl alcohols), or partly branched such as the  
Lutensols, Dobanols and Neodols which have about 25% 2-methyl branching  
(Lutensol being a Trade Name of BASF, Dobanol and Neodol being Trade  
15 Names of Shell), or Synperonics, which are understood to have about 50%  
2-methyl branching (Synperonic is a Trade Name of I.C.I.) or the primary  
alcohols having more than 50% branched chain structure sold under the  
Trade Name Lial by Liquichimica. Specific examples of nonionic  
surfactants falling within the scope of the invention include Dobanol  
20 45-4, Dobanol 45-7, Dobanol 45-9, Dobanol 91-2.5, Dobanol 91-3, Dobanol  
91-4, Dobanol 91-6, Dobanol 91-8, Dobanol 23-6.5, Synperonic 6,  
Synperonic 14, the condensation products of coconut alcohol with an  
average of between 5 and 12 moles of ethylene oxide per mole of alcohol,  
the coconut alkyl portion having from 10 to 14 carbon atoms, and the  
25 condensation products of tallow alcohol with an average of between 7 and  
12 moles of ethylene oxide per mole of alcohol, the tallow portion  
comprising essentially between 16 and 22 carbon atoms. Secondary linear  
alkyl ethoxylates are also suitable in the present compositions,  
especially those ethoxylates of the Tergitol series having from about 9  
30 to 15 carbon atoms in the alkyl group and up to about 11, especially from  
about 3 to 9, ethoxy residues per molecule.

The compounds formed by condensing ethylene oxide with a hydrophobic  
base formed by the condensation of propylene oxide with propylene  
glycol. The molecular weight of the hydrophobic portion generally falls  
35 in the range of about 1500 to 1800. Such synthetic nonionic detergents  
are available on the market under the Trade Name of "Pluronic" supplied  
by Wyandotte Chemicals Corporation.

Cationic surfactants suitable for use herein include quaternary ammonium surfactants and surfactants of a semi-polar nature, for example amine oxides.

$$\text{R}^1 - \text{N}^+ \begin{array}{c} \text{R}^2 \\ | \\ \text{O}^- \end{array} \left[ \text{---} (\text{CH}_2)_i \text{---} \text{N}^+ \begin{array}{c} \text{R}^2 \\ | \\ \text{O}^- \end{array} \right]_j \text{R}^2 \quad \text{VIII}$$

In a preferred embodiment  $R^1$  has from 10 to 16 carbon atoms and each  $R^2$  is independently selected from methyl and  $-(C_nH_{2n}O)_m$  wherein  $m$  is from 1 to 3 and the sum total of  $C_nH_{2n}O$  groups in a molecule is no more than 5, preferably no more than 3. In a highly preferred embodiment,  $j$  is 0 and each  $R^2$  is methyl, and  $R^1$  is  $C_{12}$ - $C_{14}$  alkyl.

$$\begin{array}{c} \text{R}^4 \\ | \\ \text{R}^3 - \text{N}^+ \\ | \\ \text{R}^4 \end{array} \left[ \begin{array}{c} | \\ | \\ | \end{array} \right] - (\text{CH}_2)_i - \begin{array}{c} \text{R}^4 \\ | \\ \text{N}^+ \\ | \\ \text{R}^4 \end{array} \left[ \begin{array}{c} | \\ | \\ | \end{array} \right] \begin{array}{c} \text{R}^4 \\ | \\ \text{R}^4 \end{array} \quad \text{Z} \quad \text{IX}$$

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wherein  $R^3$  is a linear or branched alkyl, alkenyl or alkaryl group having 10 to 16 carbon atoms and each  $R^4$  is independently selected from  $C_{1-4}$  alkyl,  $C_{1-4}$  alkaryl and  $-(C_nH_{2n}O)_m$  wherein  $i$  is an integer from 1 to 6,  $j$  is 0 or 1,  $n$  is 2 or 3 and  $m$  is from 1 to 7, the sum total of  $C_nH_{2n}O$  groups in a molecule being no more than 7, and wherein  $Z$  represents counteranion in number to give electrical neutrality.

In a preferred embodiment,  $R^3$  has from 10 to 14 carbon atoms and each  $R^4$  is independently selected from methyl and  $(C_nH_{2n}O)_m$  wherein  $m$  is from 1 to 3 and the sum total of  $C_nH_{2n}O$  groups in a molecule is no more than 5, preferably no more than 3. In a highly preferred embodiment  $j$  is 0,  $R^4$  is selected from methyl, hydroxyethyl and hydroxypropyl and  $R^3$  is  $C_{12}-C_{14}$  alkyl. Particularly preferred surfactants of this class include  $C_{12}$  alkyl trimethylammonium salts,  $C_{14}$  alkyltrimethylammonium salts, coconutalkyltrimethylammonium salts, coconutalkyldimethyl-hydroxyethylammonium salts, coconutalkyldimethylhydroxy-propylammonium salts, and  $C_{12}$  alkyldihydroxyethylmethyl ammonium salts.

As mentioned previously, the suds-suppressor compositions are particularly advantageous in detergent compositions containing a high level of deterative surfactant (at least 12%) wherein the surfactant is based completely or in part on anionic or cationic surfactants having from 10 to 16 carbon atoms. In preferred compositions therefore,  $C_{10-16}$  anionic and/or cationic surfactants constitute from about 5% to 100%, preferably from about 10% to about 50% by weight of the total deterative surfactant mixture.

In preferred embodiments, the detergent compositions of the invention also comprise from about 0.2% to 3%, preferably from about 0.5% to about 1.5% of  $C_{16}-C_{24}$  fatty acid or fatty acid soap. This acts in combination with the suds-suppressor system to provide improved suds-suppression robustness.

Suitable fatty acid soaps can be selected from the ordinary alkali metal (sodium, potassium), ammonium, and alkylammonium salts of fatty acids containing from about 16 to about 24 and preferably from about 18 to about 22 carbon atoms in the alkyl chain. Suitable fatty acids can be obtained from natural sources such as, for instance, from soybean oil,

castor oil, tallow, whale and fish oils, grease, lard and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Napthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from tallow and hydrogenated fish oil, as well as the free fatty acids themselves.

The detergent compositions of the invention can also contain up to about 90%, preferably from about 15% to about 60% of detergency builder. Suitable detergent builders useful herein can be of the polyvalent inorganic and polyvalent organic types, or mixtures thereof. Non-limiting examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, sesquicarbonates, borates, phosphates, pyrophosphates, tripolyphosphates and bicarbonates. "Seeded carbonate" builders as disclosed in BE-A-798,856 are also suitable.

Examples of suitable organic alkaline detergency builder salts are water-soluble polycarboxylates such as the salts of nitrilotriacetic acid, lactic acid, glycollic acid and ether derivatives thereof as disclosed in BE-A-821,368, 821,369 and 821,370; succinic acid, malonic acid, (ethylenedioxy)diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid; citric acid, aconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxy-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propanetetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclopentane cis, cis,cis-tetracarboxylic acid, cyclopentadienide pentacarboxylic acid, 2,3,4,5-tetra hydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetra-hydro-furan-cis-di-carboxylic acid, 1,2,3,4,5,6-hexane-hexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in GB-A-1,425,343.



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Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in CA-A-755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

5 A further class of builder is the insoluble aluminosilicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation  $\text{Na}_z(\text{AlO}_2)_z(\text{SiO}_2)_y \cdot x\text{H}_2\text{O}$  wherein  $z$  and  $y$  are integers of at least 6, the molar ratio of  $z$  to  $y$  is in the range from 1.0 to about 0.5 and  $x$  is an integer from about 15 to about 264.  
10 Compositions incorporating builder salts of this type form the subject of GB-A-1,429,143, DE-A-2,433,485, and DE-A-2,525,778

An alkali metal, or alkaline earth metal, silicate can also be present. The alkali metal silicate is preferably from about 3% to about 15%. Suitable silicate solids have a molar ratio of  $\text{SiO}_2/\text{alkali metal}_2\text{O}$  in the range from about 1.0 to about 3.3, more preferably from 1.5 to 2.0.

The compositions of the invention can be supplemented by all manner of detergent and laundering components, inclusive of bleaching agents, enzymes, fluorescers, photoactivators, soil suspending agents, anti-caking agents, pigments, perfumes, fabric conditioning agents etc.

Enzymes suitable for use herein include those discussed in US-A-3,519,570 and US-A-3,533,139. Suitable fluorescers include Blankophor MBH (Bayer AG) and Tinopal CBS and EMS (Ciba Geigy).

25 Photoactivators are discussed in EP-A-57088, highly preferred materials being zinc phthalocyanine, tri- and tetra-sulfonates. Suitable fabric conditioning agents include smectite-type clays as disclosed in GB-A-1400898 and di- $\text{C}_{12}$ - $\text{C}_{24}$  alkyl or alkenyl amines and ammonium salts.

30 Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756  
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incorporated herein by reference. Preferred polymers include copolymers or salts thereof of maleic anhydride with ethylene, methylvinyl ether, acrylic acid or methacrylic acid, the maleic anhydride constituting at least about 20 mole percent of the copolymer. These polymers are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Peroxygen bleaching agents suitable for use in the present compositions include hydrogen peroxide, inorganic peroxides, peroxy salts and hydrogen peroxide addition compounds, and organic peroxides and peroxy acids. Organic peroxyacid bleach precursors (bleach activators) can additionally be present.

Suitable inorganic peroxygen bleaches include sodium perborate mono- and tetrahydrate, sodium percarbonate, sodium persulfate, urea-hydrogen peroxide addition products and the clathrate  $4\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2 \cdot 1\text{NaCl}$ . Suitable organic bleaches include peroxy lauric acid, peroxy octanoic acid, peroxy nonanoic acid, peroxy decanoic acid, diperoxy dodecanedioic acid, diperoxy azelaic acid, mono- and diperoxy phthalic acid and mono- and diperoxy isophthalic acid. Peroxyacid bleach precursors suitable herein are disclosed in UK-A-2040983, preferred being peracetic acid bleach precursors such as tetraacetylene diamine, tetraacetylmethylenediamine, tetraacetylhexylenediamine, sodium p-acetoxybenzene sulphonate, tetraacetylglycouril, pentaacetylglucose, octaacetyllactose, and methyl O-acetoxy benzoate. The higher acyl derivatives disclosed in EP-A-98129 and European Patent Application 843010703 are also highly suitable, especially the  $\text{C}_6\text{-C}_{10}$  acyl oxybenzene sulphonates and carboxylates such as sodium 3,5,5-trimethyl hexanoyl oxybenzene sulphonate. Bleach activators can be added at a weight ratio of bleaching agent to bleach activator in the range from about 40:1 to about 4:1.

In the Examples which follow, the abbreviations used have the following designations:-

- 5           LAS               : Linear C<sub>11.8</sub> alkyl benzene sulphonate.
- TAE(n)           : Hardened tallow alcohol ethoxylated with n moles  
                                  of ethylene oxide.
- MAO               : C<sub>12-14</sub> alkyl dimethylamine oxide.
- AS                : C<sub>12-14</sub> alcohol sulfate, sodium salt.
- TAS               : Tallow alcohol sulfate
- CATAB            : Coconut alkyl trimethyl ammonium bromide.
- 10          Dobanol 45-E-7 : A C<sub>14-15</sub> oxo-alcohol with 7 moles of ethylene  
                                  oxide, marketed by Shell.
- TAED             : Tetraacetyl ethylene diamine.
- Silicate         : Sodium silicate having an SiO<sub>2</sub>:Na<sub>2</sub>O ratio of  
                                  1.6:1.
- 15          Gantrez AN119 : Trade Name for maleic anhydride/vinyl methyl ether  
                                  co-polymer, believed to have an average molecular  
                                  weight of about 240,000, marketed by GAF. This  
                                  was prehydrolysed with NaOH before addition.
- 20          MA/AA           : Copolymer of 1:4 maleic acid/acrylic acid,  
                                  average molecular weight about 80,000.
- Brightener       : Disodium 4,4'-bis(2-morpholino-  
                                  4-anilino-s-triazino-6-ylamino)stilbene-2:2'-disulphate.

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- Dequest 2060 : Trade Name for diethylenetriamine-penta(methylenephosphonic acid), marketed by Monsanto.
- Dequest 2041 : Trade Name for ethylenediamine tetra(methylene phosphonic acid)monohydrate, marketed by Monsanto.
- INOBS : Sodium 3,5,5-trimethyl hexanoyl oxybenzene sulphonate.
- Perborate : Sodium perborate tetrahydrate.
- DC 198 : Alkoxylated siloxane containing oxyethylene and oxypropylene groups, marketed by Dow Corning.
- Silicone/Silica : 85:15 by weight high shear mix of polydimethylsiloxane and silanated silica, particle size 10 to 20 millimicrons, viscosity as indicated.
- H.V. Silicone : Polydimethylsiloxane, viscosity 60,000 cs.
- Enzyme : Protease.

The present invention is illustrated by the following non-limiting examples:-

EXAMPLES I TO V

Granular detergent compositions are prepared as follows. A base powder composition is first prepared by mixing the indicated components in a crutcher as an aqueous slurry at a temperature of about 80°C and containing about 35% water. The slurry is then spray dried at a gas inlet temperature of about 300°C to form base powder granules. Suds suppressor composition is then prepared by premixing the silicone/silica high shear mix and the high viscosity silicone, adding the premix to a melt of the ethoxylated tallow alcohol, adding the silicone/silica dispersing agent and spraying the dispersion onto sodium tripolyphosphate in a fluidized bed. Finally, the base powder composition is dry mixed with suds suppressor, enzyme and bleach components, and additional nonionic surfactant and fatty acid, where present, are sprayed onto the total mixture.

All percentages are given by weight of total detergent composition.

EXAMPLES

		I	II	III	IV	V
	<u>BASE POWDER</u>					
20	IAS	6	4	10	5	8
	AS	4	2	2	5	-
	MAO	-	-	-	-	1
	CATAB	-	-	2	-	1
	Gantrez AN119	-	1	-	-	1
25	Silicate	6	7	5	5	10
	Sodium carbonate	-	8	-	13	5
	MA/AA	0.5	-	1	2	-
	Brightener	0.2	0.3	0.1	0.2	0.2
	Dequest 2060	-	-	0.3	-	-
30	Dequest 2041	0.1	0.3	-	0.3	0.1
	EDTA	0.2	0.3	-	0.2	0.2
	Sodium tripolyphosphate	32	24	28	25	30
	Magnesium sulphate (ppm)	1000	-	800	1000	1200
	Sodium sulphate, moisture &					
35	miscellaneous	-----to 100-----				

SUDS SUPPRESSOR

TAE(25)	0.6	0.37	0.5	-	-
TAE(80)	-	-	-	0.72	0.7
PEG 6000	-	-	0.5	-	-
H.V. Silicone	0.3	0.25	0.25	0.18	0.28
Silicone/silica(10,000 cs)	0.3	0.12	0.25	0.18	0.14
DC198	0.05	0.03	0.08	0.04	0.06
Sodium tripolyphosphate	1.75	1.55	3.42	1.88	2.32

OTHER ADDITIVES

Enzyme	0.4	-	1.0	0.5	0.6
Sodium perborate tetrahydrate	24	12	14	21	22
TAED	-	2	1	-	-
INOB	2	-	-	4	-
Dobanol 45-E-7	5	10	-	2	4
C <sub>18-22</sub> fatty acid	1	1.5	-	1	-

The above products combine excellent detergency performance together with improved foam regulation characteristics across the range of wash temperature, product usage, soil, load and rinsing conditions.

EXAMPLES VI TO X

Granular detergent compositions are prepared as follows. Base powder compositions are first prepared as described in Examples I to V. Suds suppressor compositions are then prepared by mixing the first and second organic carrier components (TAE(80) and Dobanol 45-E-7 respectively) together with the siloxane-oxyalkylene copolymer dispersing agent, premixing the silicone/silica high shear mix and the

high viscosity silicone, high shear mixing the premix with the organic carrier component, dry mixing the base powder compositions with enzyme and bleach components and spraying the suds suppressor compositions onto the total dry mix.

All percentages are given by weight of total composition.

EXAMPLES

BASE POWDER

	VI	VII	VIII	IX	X
LAS	5	12	7	10	5
TAS	5	1	2	1	1
Gantrez AN119	-	1	-	0.8	1
Silicate	5	7	6	4	9
MA/AA	2	-	1	0.4	-
Brightener	0.2	0.3	0.1	0.5	0.2
Dequest 2060	-	-	0.3	0.2	-
Dequest 2041	0.3	0.3	-	-	0.1
EDTA	0.2	0.3	-	0.1	0.2
Sodium tripolyphosphate	23	24	32	32	30
Sodium carbonate	13	-	5	8	-
Magnesium sulphate (ppm)	1000	-	800	-	1200
Sodium sulphate, moisture & miscellaneous					

to 100

SUDS SUPPRESSOR COMPOSITION

Dobanol 45-E-7	3.5	0.7	6	2	12
TAE (80)	0.5	0.5	1	0.4	1
DC-198	0.03	0.033	0.35	0.02	0.05
Silicone/Silica (6,500 cs)	0.11	0.15	0.15	0.11	0.19
HV Silicone	0.22	0.15	0.2	0.11	0.38

OTHER ADDITIVES

Enzyme	0.6	-	1.2	-	0.9
Sodium perborate tetrahydrate	20	12	15	28	22
TAED	0.5	-	1	-	-
INOS	2.5	-	-	3.5	-

The above products combine excellent detergency performance together with improved foam regulation characteristics across the range of wash temperature, product usage, soil, load and rinsing conditions.



CLAIMS

1. A suds suppressor composition characterized by:

(a) a suds suppressor system comprising a blend of

(i) a high shear mix of polydimethylsiloxane and hydrophobic silica suds suppressing agents in a weight ratio of polydimethylsiloxane:hydrophobic silica in the range from about 75:25 to about 99:1, the polydimethylsiloxane having a viscosity at 25°C in the range from about 20 to about 12,500 cs, and

(ii) polydimethylsiloxane suds suppressing agent having a viscosity at 25°C of at least about 25,000 cs wherein the blend of high shear mix and high viscosity polydimethylsiloxane has a viscosity at 25°C of at least about 18,000 cs, the suds suppressor system being dispersed in:

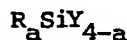
(b) a water-soluble or water-dispersible organic carrier comprising:

(i) from about 1% to 100% by weight thereof of a first organic carrier component having a melting point in the range from about 38°C to about 90°C, and

(ii) from 0% to about 99% by weight thereof of a second organic carrier component selected from ethoxylated nonionic surfactants having a hydrophilic-lipophilic balance (HLB) in the range from about 9.5 to about 13.5 and a melting point in the range from about 5°C to about 36°C.

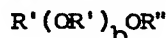
2. A composition according to Claim 1 characterized in that the high shear mix is a mixture of polydimethylsiloxane having a viscosity at 25°C in the range from 100 to 4000cs and hydrophobic silica in a weight ratio of from about 80:20 to about 95:5.

3. A composition according to Claim 1 or 2 characterized in that the high viscosity polydimethylsiloxane has a viscosity at 25°C of at least about 30,000 cs preferably from about 50,000 cs to about 100,000 cs and the blend of high shear mix and high viscosity polydimethylsiloxane has a viscosity at 25°C of at least about 20,000 cs, preferably from about 25,000 cs to about 60,000 cs.
4. A composition according to any of Claims 1 to 3 characterized in that the high shear mix and high viscosity polydimethylsiloxane are in a weight ratio of from about 4:1 to about 1:4, preferably from about 2:1 to about 1:3.
5. A composition according to any of Claims 1 to 4 characterized in that the first carrier component comprises an ethoxylated nonionic surfactant having an HLB in the range from about 15 to about 19, preferably from about 17 to about 19 and a melting point in the range from about 38°C to 60°C preferably from about 40°C to about 55°C.
6. A composition according to any of Claims 1 to 5 characterized in that it additionally comprises a siloxane-oxyalkylene copolymer dispersing agent having the general formula I.



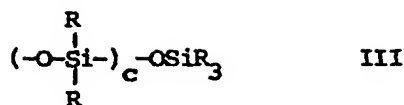
I

wherein a is 0 or an integer from 1 to 3, R is an alkyl group containing from 1 to 30 carbon atoms, or a group of formula II:



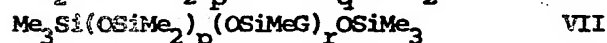
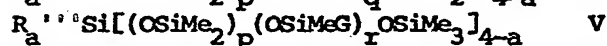
II

wherein R' is an alkylene group containing from 1 to 6 carbon atoms, b has a value of from 1 to 100; and R'' is a capping group which is selected from hydrogen, alkyl, acyl, aryl, alkaryl, aralkyl or alkenyl groups containing up to 20 carbon atoms, sulfate, sulfonate, phosphate, carboxylate, phosphonate, borate or isocyanate groups, or mixtures thereof; Y is a group having the formula III:-



wherein R is as defined above and c has a value from 1 to 200;  
wherein at least one R group in the compound has the formula II;  
and wherein the weight ratio of dispersing agent to  
polydimethylsiloxane is from about 1:4 to about 1:40, preferably  
from about 1:6 to about 1:20.

7. A composition according to Claim 6 characterized in that the  
siloxane-oxyalkylene copolymer is selected from copolymers having  
the general formula IV to VII



wherein R''' is a C<sub>1-10</sub> alkyl group, Me is methyl, G is the group  
of formula II, a has a value of 0 or 1, p has a value of at least  
1, q has a value of 0 to 50 and r has a value of 1 to 50.

8. A composition according to any of Claims 1 to 7 characterized in  
that the weight ratio of first carrier component:suds suppressor  
system is from 10:1 to 1:5.
9. A composition according to any of Claims 1 to 8 in granular form  
characterized in that the carrier consists essentially of the first  
carrier component.
10. A composition according to Claim 9 characterized additionally by  
from 25% to 95%, preferably from 50% to 85% thereof of a solid  
inorganic diluent.

11. A composition according to any of claims 1 to 8 characterized in that the carrier comprises from about 1% to about 50%, preferably from about 2% to about 25% by weight thereof of the first carrier component, and from about 50% to about 99%, preferably from about 75% to about 98% by weight thereof of the second carrier component.
12. A granular detergent composition characterized by
  - (a) from about 3% to about 60%, preferably from about 12% to about 50% of non-soap, deterative, organic surfactant selected from anionic, nonionic, ampholytic, zwitterionic and cationic surfactants and mixtures thereof, and
  - (b) from about 0.1 to about 10%, preferably from about 0.5 to about 5% of a granular suds suppressor composition according to Claim 9 or 10.
13. A granular detergent composition characterized by:
  - (a) from about 30% to about 99.5% of base granules comprising from about 3% to about 30%, preferably from about 5% to about 20% of non-soap organic surfactant selected from anionic and cationic surfactants and mixtures thereof, and
  - (b) from about 0.5% to about 30%, preferably from about 3% to about 20% of a suds suppressor composition according to claim 11 sprayed in fluent form onto at least a portion of the base granules.
14. A composition according to Claim 12 or 13 characterized in that the organic surfactant comprises a water-soluble C<sub>10-16</sub> alkyl, alkenyl or alkaryl anionic or cationic surfactant.
15. A composition according to any of Claims 12 to 14 characterized additionally by from about 0.2% to about 3%, preferably about 0.5% to about 1.5% of C<sub>16</sub>-C<sub>24</sub> fatty acid or fatty acid soap.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0142910

Application number

EP 84 30 5682

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	EP-A-0 046 342 (PROCTER & GAMBLE CO.) * Claims 1-5 *		C 11 D 3/00 C 11 D 3/12 C 11 D 3/37
A	US-A-4 264 465 (H. ABEL) * Claims 1-10 *		
A	EP-A-0 013 028 (HENKEL KGAA) * Claims 1-5 *		
A,P	EP-A-0 091 802 (PROCTER & GAMBLE CO.) * Claims 1-7 *		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 11 D 3/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 19-11-1984	Examiner SCHULTZE D
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

